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Synthesis of Molybdenum (VI) Neopentylidene Neopentylidyne Complexes

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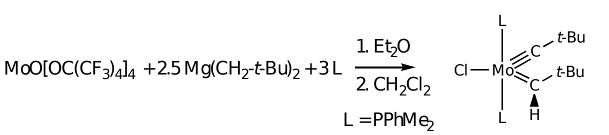
ABSTRACT: Mo(C-*t*-Bu)(CH-*t*-Bu)(Cl)(PMe_2Ph)$_2$ (**1**) was prepared as off-white crystals in 26% yield through addition of 2.5 equiv of Mg(CH_2-*t*-Bu)$_2$ to Mo(O)[OC(CF_3)$_3$]$_4$ in diethyl ether followed by three equivalents of PMe_2Ph and a workup that includes dichloromethane (the source of Cl). Compound **1** is largely a *syn* isomer initially that equilibrates to give approximately a 1:1 mixture of *syn* and *anti* isomers within 1-2 hours. Compound **1** reacts with Li(3,5-dimethylpyrrolide) to give Mo(C-*t*-Bu)(CH-*t*-Bu)(η^1-Me_2Pyr)(PMe_2Ph)$_2$ (**2a**) as a pale yellow solid in 76% yield, and **2a** reacts with Ph_3SiOH to give a mixture of *syn* and *anti* Mo(C-*t*-Bu)(CH-*t*-Bu)($OSiPh_3$)(PMe_2Ph)$_2$ (**3a**) in 84% yield. All three compounds tend to lose PMe_2Ph to give 14e monophosphine complexes with the formulae Mo(C-*t*-Bu)(CH-*t*-Bu)(X)(PMe_2Ph) (X = Cl, Me_2Pyr, or $OSiPh_3$), none of which could be isolated. X-ray studies show the structures of **1**, **2a**, and **3a** to be analogous with τ values of 0.45, 0.53, and 0.69, respectively.

Imido alkyl complexes such as M(NR')$_2$(CH_2R)$_2$ (M = Mo or W; R' = aryl, t-butyl, or adamantyl and CH_2R = neopentyl or neophyl), which can be prepared readily from M(NR')$_2$(dme)Cl_2 complexes and magnesium or lithium alkyls, yield M(NR')(CHR)X_2 complexes when one of the imido ligands is protonated with two equivalents of HX (e.g., X = triflate).[1] However, analogous approaches to oxo alkylidene complexes usually are thwarted by the fact that oxo ligands are attacked by the alkylating agent and removed from the metal. Attempted alkylations of Mo oxo complexes more often give rise to low yields of oxo products, or none at all. For example, Osborn reported the synthesis of Mo(O)(CH_2-*t*-Bu)$_3$Cl and "Mo(O)(CH_2-*t*-Bu)$_4$" through addition of Mg(CH_2-*t*-Bu)$_2$ to Mo(O)Cl_4,[2] but experimental details (including yields) were not provided in either of the succinct reports, and Mo(O)(CH_2-*t*-Bu)$_4$ had to be reformulated (as noted in footnote 1 in reference 2b, without further details) as Mo(O)(CH_2-*t*-Bu)$_3$(OCH_2-*t*-Bu). The neopentoxide in Mo(O)(CH_2-*t*-Bu)$_3$(OCH_2-*t*-Bu) could arise through attack by the alkylating agent on the oxo ligand.[3] It also has been reported that addition of six equivalents of (*t*-BuCH_2)MgCl to MoO_2Cl_2 in diethyl ether gives the best reported yield (~35%) of Mo(C-*t*-Bu)(CH_2-*t*-Bu)$_3$.[4] The analogous trimethylsilylmethylidyne complex, Mo($CSiMe_3$)(CH_2SiMe_3)$_3$ (8% yield; liquid at 22 °C) has been prepared similarly with (Me_3SiCH_2)$_3$Mo≡Mo(CH_2SiMe_3)$_3$ (25% yield; crystalline) and unstable (Me_3SiCH_2)$_3$Mo=$CHSiMe_3$ (proposed) being two other metal-containing products.[5]

One exception to low yield alkylations of Mo oxo complexes is the class of molybdenum or tungsten compounds with the formula MO_2(CH_2R)$_2$(bipy) (CH_2R can be a variety of alkyls, including neopentyl), which can be prepared through alkylation of MO_2Cl_2(bipy) compounds with Grignard reagents.[6] The final M(VI) complexes are formed only after exposure of the crude product to water and air, so it appears likely that at least some, if not most, of the metal is reduced and then reoxidized in the presence of water and air. WO_2(CH_2-*t*-Bu)$_2$(bipy) is a precursor to W(O)(CH-*t*-Bu)Cl_2L_2 upon reaction of WO_2(CH_2-*t*-Bu)$_2$(bipy) with Me_3SiCl, $ZnCl_2$, and two equivalents of L (e.g., L = $PPhMe_2$); W(O)(CH_2-*t*-Bu)$_2Cl_2$(bipy) is a plausible intermediate.[7] This approach to the synthesis of Mo(O)(CH-*t*-Bu)Cl_2L_2 complexes failed in our hands so far. A second exception is the reaction between Mo(O)(Cl)$_2$(*t*-Bu_3P=N)$_2$ and two equivalents of $LiCH_2SiMe_3$ to give Mo(O)($CHSiMe_3$)(*t*-Bu_3P=N)$_2$ in 87% yield;[8] Mo(O)(CH_2SiMe_3)$_2$(*t*-Bu_3P=N)$_2$ is the plausible intermediate in this reaction. Unfortunately, Mo(O)($CHSiMe_3$)(*t*-Bu_3P=N)$_2$ and analogous molybdenum imido alkylidene complexes that contain two *t*-Bu_3SiO^- ligands (which are sterically approximately equivalent to *t*-Bu_3P=N^- ligands)[9] are relatively unreactive in olefin metathesis reactions.

We recently prepared molybdenum oxo alkylidene complexes through a controlled addition of one equivalent of water to molybdenum(VI) $OC(CF_3)_3$ or $OC(CF_3)_2Me$ benzylidyne complexes.[10] In the hope that more direct routes to these Mo oxo alkylidene complexes could be successful we turned to alkylation of $Mo(O)[OC(CF_3)_3]_4$.[11] Yellow $Mo(O)[OC(CF_3)_3]_4$ can be prepared readily from $Mo(O)Cl_4$ and four equiv of $NaOC(CF_3)_3$. It can be sublimed under a good vacuum ($<10^{-2}$ mm) at 60-80 °C. It is poorly soluble in organic solvents (pentane, benzene, toluene) but partially soluble in diethyl ether or dichloromethane.

We decided to explore alkylation of $Mo(O)[OC(CF_3)_3]_4$ with $Mg(CH_2$-*t*-$Bu)_2$ in the presence of PMe_2Ph in order to trap any monometallic products. Alkylation reactions using 0.5, 1.0, 2.0, and 2.5 equiv of $Mg(CH_2CMe_3)_2$ in the presence of PMe_2Ph in diethyl ether were explored initially. Each crude sample was dissolved in C_6D_6 or CD_2Cl_2 and examined by proton and/or ^{31}P NMR. A small multiplet in the region characteristic of a molybdenum alkylidene having two phosphines bound to the metal in proton NMR spectra in CD_2Cl_2 grew slightly over a day, but no other product could be identified. When 2.5 equivalents of $Mg(CH_2CMe_3)_2$ were used and CH_2Cl_2 was part of the workup, the alkylidene could be extracted into pentane and crystallized reproducibly from a concentrated pentane solution at -20 °C as off-white needles in a yield of ~25%. When the crude brown residue was dissolved in C_6D_6 and not exposed to dichloromethane, no alkylidene resonance was observed, even after addition of two equivalents of PMe_2Ph. However, when a drop of CD_2Cl_2 was added to this sample, the alkylidene resonance grew in with time. The *syn* alkylidene resonance can be observed in the ^1H NMR spectrum five hours after addition of CD_2Cl_2 and stops increasing after ~60 hours. There was no further change in the ^1H NMR spectrum.



(1)

1 (26%)

An X-ray structural study confirms that **1** is the "Ene/Yne" complex, Mo(C-*t*-Bu)(CH-*t*-Bu)$(PPhMe_2)_2$Cl (**1**; eq 1 and Figure 1), not an oxo alkylidene complex. The overall geometry is approximately halfway between a TBP and a SP (τ^{12} = 0.45), although **1** (and related derivatives described below) will be drawn as a TBP with L in the apical positions for convenience. The bond lengths and angles (Table 1) are not unusual for neopentylidyne ligands (1.691(3) Å, 166.80°) or *syn* neopentylidene ligands (1.985(3) Å, 152.57°). The chloride must come from dichloromethane, a phenomenon that has been reported in the literature for certain Mo[13a,b] and Re[13c] compounds. No mechanistic details have been reported for formation of chloride complexes in the presence of dichloromethane and we also do not want to propose any for forming **1** at this stage.

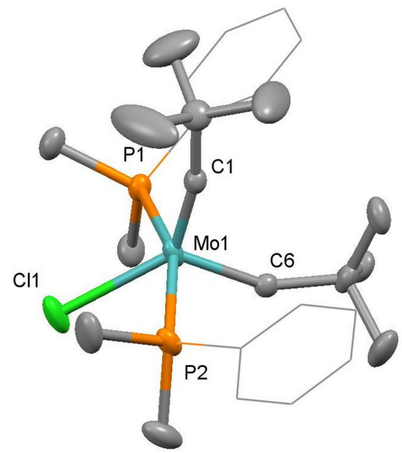


Figure 1. Structure of **1** (τ = 0.45).

Compound **1** is related to tantalum bisneopentylidene complexes (e.g., Ta(CH-*t*-Bu)$_2(PMe_3)_2$Cl) which contain two different neopentylidene ligands, one of which has a significantly greater agostic interaction of its alkylidene CH_{α} bond with the metal than does the other.[14] It also is related to W(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)(PMe_3)_2$,[15] square pyramidal W(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu)(dmpe),[15] and trimethylsilyl relatives.[16] The alkylidene is in the *syn* orientation in the crystal chosen for the X-ray study. Compound **1** is stable in benzene solution for several days at temperatures as high as 80 °C. Attempts to remove one of the phosphines from a C_6D_6 solution of **1** through addition of one equivalent of $B(C_6F_5)_3$ to **1** in 0.5 mL C_6D_6 (0.04 M) led only to decomposition to unidentified products. We propose that loss of phosphine in the solid state at 1 atm is the reason for a failure to obtain satisfactory elemental analyses for **1** and related derivatives **2a** and **3a** described below.

Table 1. Selected bond lengths and angles in **1**, **2a**, and **3a**.

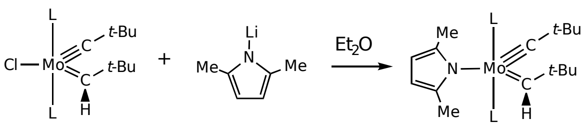
	1	**2a**	**3a**
Mo1-C1	1.691(3)	1.661(11)	1.764(6)
Mo1-C6	1.985(3)	2.000(9)	1.9214(14)
Mo1-P1	2.5089(3)	2.5092(10)	2.5202(3)
Mo1-P2	2.5196(3)	2.5092(10)	2.5366(4)
Mo1-C1-*t*-Bu	166.80	172.59	170.61
Mo1-C6-*t*-Bu	152.57	151.52	152.16
P1-Mo1-P2	160.28	164.97	171.25
C1-Mo1-C6	104.33	102.49	103.51

Mo1-X[a]	2.5197(3)	2.227(3)	2.0748(9)

[a] X = Cl (in **1**), N (in **2a**), or O (in **3a**).

Proton NMR spectra of **1** usually show two multiplet alkylidene resonances at 13.87 ppm (*anti*, $^1J_{CH}$ = 137.0 Hz) and 12.26 ppm (*syn*, $^1J_{CH}$ = 100.6 Hz). Freshly isolated **1** is usually *syn*-rich, occasionally as high as 95% *syn* (see SI). Upon recrystallizations of **1**, the *syn*:*anti* ratio approaches 1:1 and remains so.

Compound **1** reacts with Li(2,5-dimethylpyrrolide) to yield the monopyrrolide complex, **2a** (eq 2). Compound **2a** can be crystallized from pentane as off-white needles in 76% yield. An X-ray study showed the structure of **2a** (Fig 2) to be analogous to that of **1**, with the pyrrolide bound to the metal in an η^1 fashion. The overall geometry and bond lengths and angles in **2a** are similar to those found in **1** (Table 1).



(2)

2a (76%)

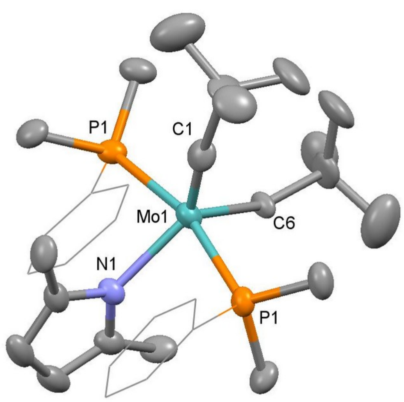
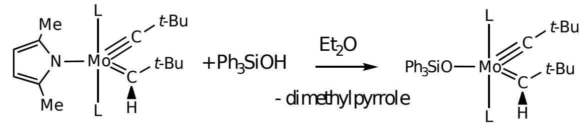


Figure 2. Structure of **2a** (τ = 0.53).

In ^{1}H NMR spectra of pure samples of **2a**, two *syn* alkylidene resonances are found, one triplet (at 11.65 ppm in C_6D_6) for **2a** and one doublet (~10% of the total at 13.48 ppm in C_6D_6). We ascribe the latter to a monophosphine complex, Mo(C-*t*-Bu)(CH-*t*-Bu)($PPhMe_2$)(Me_2Py) (**2b**). Compounds **2a** and **2b** (plus phosphine) are in equilibrium at room temperature; in a sample of 0.033 M **2a** in C_6D_6 K_{eq} was found by ^{1}H NMR spectroscopy to be 3.7x10^{-4} M at room temperature. The ^{31}P NMR of a sample of **2a** in C_6D_6 at room temperature shows three resonances at 30.4, 7.3, and -46.5 ppm for **2b**, **2a**, and free phosphine, respectively. The magnetization exchange rates between these two species were measured through a series of 1D EXSY experiments at different temperatures (> 40 °C). For dissociation of phosphine from **2b** $\Delta H^‡$ was found to be 121 (±8) kJ/mol and $\Delta S^‡$ was found to be 0.095 (±0.026) kJ/molK. For the reverse reaction $\Delta H^‡$ and $\Delta S^‡$ were found to be 76(±5) kJ/mol and -0.028 (±0.017) kJ/molK, respectively. **2b** was also the major product in an NMR-scale reaction in C_6D_6 of **2a** with 1 equiv of $B(C_6F_5)_3$ (see SI).



(3)

2a **3a** (84%)

Compound **2a** reacts cleanly with one equiv of triphenylsilanol to generate **3a** (eq 3). An X-ray study shows the structure of **3a** to be analogous to the structures of **1** and **2a** (Table 1 and Figure 3). An alkylidene multiplet can be observed in proton NMR spectra of **3a** at 13.29 ppm (in C_6D_6) with a $^1J_{CH}$ of 100.6 Hz that is characteristic of a *syn* alkylidene. No doublet alkylidene resonance characteristic of a monophosphine adduct can be detected by ^{1}H NMR in this case, even at temperatures up to 70 °C. Nevertheless, one of the phosphines is labile enough to be scavenged as a borane adduct upon addition of one equivalent of $B(C_6F_5)_3$ to **3a** in C_6D_6. The resulting monophosphine adduct shows a characteristics *syn* alkylidene resonance in the ^{1}H NMR spectrum at 13.32 ppm (d, J_{HP} =3.8 Hz, J_{CH}=106.1 Hz). So far we have not been able to isolate **3b**.

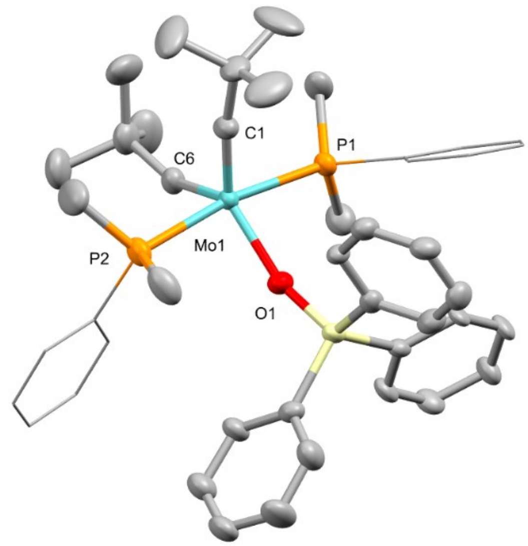


Figure 3. Structure of **3a** (τ = 0.69).

An exploratory NMR-scale ROMP reaction showed that cyclooctene was polymerized by **3a** (1%) in C_6D_6 upon addition of $B(C_6F_5)$ (1.1 equiv). The amount of cycloctene consumed was 69% in 1 h, 76% in 4 h, and 87% in 24 h.

We will seek higher yield routes to **1** and related "Ene/Yne" complexes, preferably those that do not require removal of oxo ligands from the metal and/or scavenging of chloride from dichloromethane. We are especially interested in 14e "stereogenic at metal" Mo(CR)(CH-*t*-Bu)(L)X complexes that contain a single donor (L) and anionic X, e.g., **2b** and **3b** and analogs. These are 14e relatives of (largely) imido alkylidene[1,17] and oxo[7,10] alkylidene complexes that have been explored to date as metathesis initiators. An important question is whether an alkylidyne ligand (CR) can survive unchanged in a sustained metathesis reaction, a possibility that has not been addressed to our knowledge.

ASSOCIATED CONTENT

Supporting Information Detailed NMR data and spectra for all compounds and details of X-ray studies.

Accession Codes

CCDC 1922920, 1922921, 1922922 contain the supplementary crystallographic data for **3a**, **2a**, and **1**, respectively. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

HT performed all synthetic work while PM performed all X-ray structural studies.

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Notes

The authors declare no competing financial interest.

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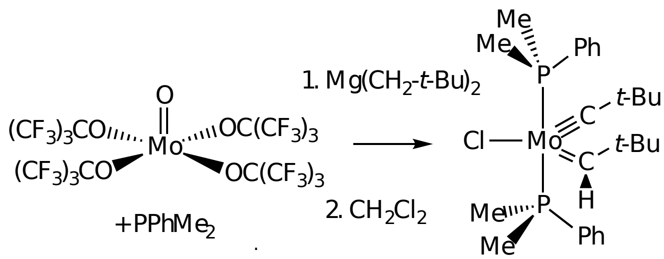
Table of Contents Artwork



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